

Changes in the Nitrogen
Constituents of Water

Maurice Elkin
W. R. Collins

1906

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Constituents of Water

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A THESIS

presented to

THE PRESIDENT and FACULTY of

THE ARMOUR INSTITUTE OF TECHNOLOGY for

THE DEGREE OF BACHELOR OF SCIENCE in

CHEMICAL ENGINEERING.

Entitled, # "CHANGES IN THE NITROGEN CONSTITUENTS OF WATER"

By

Maurice Elkin
William Randall Collins.

June 1st 1906.

Accepted

W. T. McClement

H. M. Raymond

Dean of Eng. Studies

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By
Glenn E. Collins
William Donald Collins
June 1st 1908

Accepted
W. T. McElmurray
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Dean of Eng. Div.

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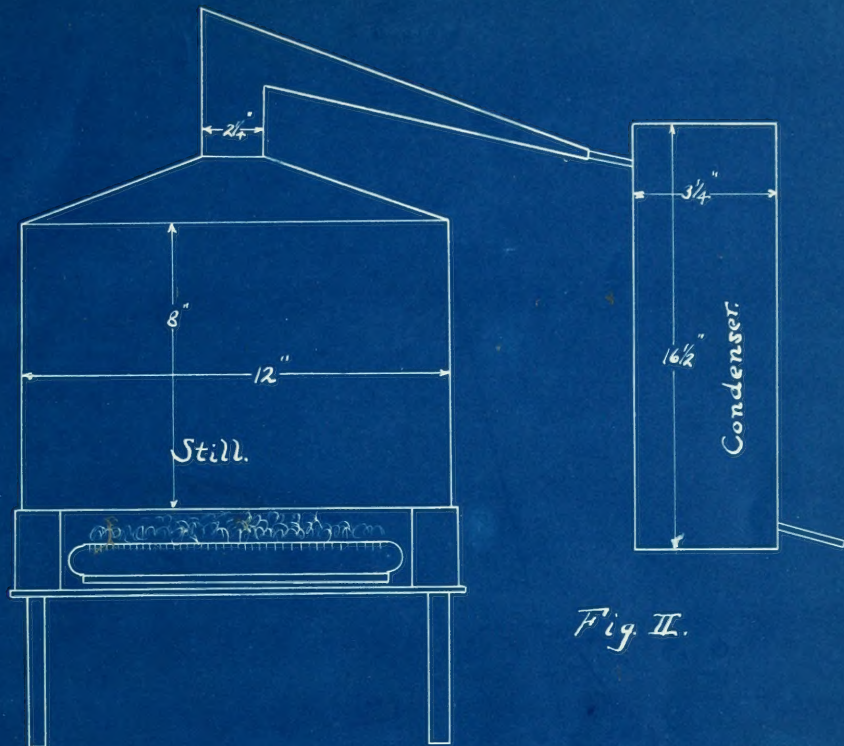


Fig. II.

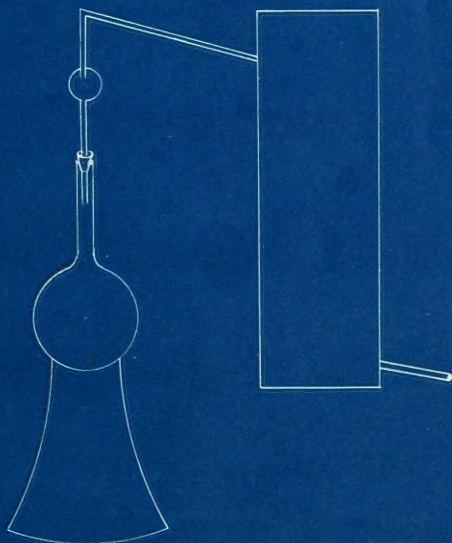


Fig. III.

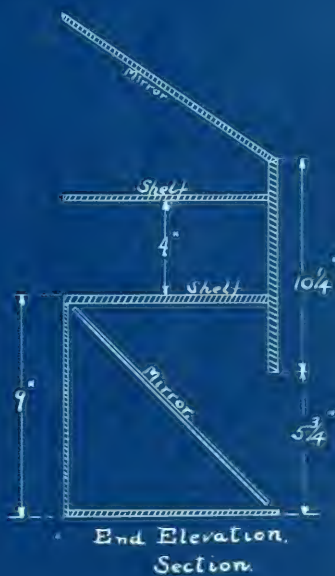
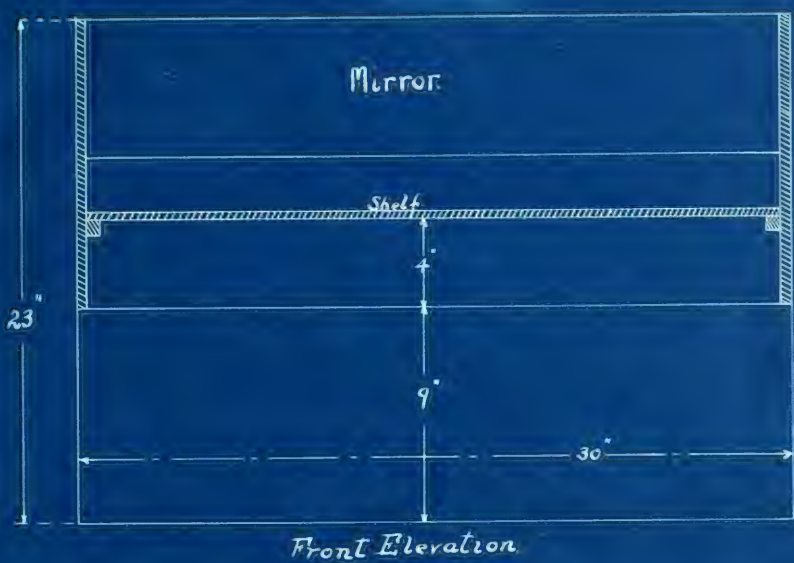


Fig. I.

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REFERENCES:

- Macoy W. P. "Examination of Water." Sanitary District of Chicago, Report of Streams Examination Journal Chem. Sec. II, 1903 p. 36.
- Fischer, "The Structure and Function of Bacteria." Mass. State Board of Health. "The Purification of Water and

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1903-1904.

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CHANGES IN THE NITROGEN CONSTITUENTS OF WATER.

It has been found in making chemical water analyses, that in order to get results which will indicate the true character of a water supply, it is necessary to make the analysis as soon after the sampling as practicable or else to keep the sample at a low temperature until the analysis is made. This is necessary because it has been found that the amounts of the constituents which are most positive indices of contamination are known to vary greatly upon standing.

Consideration of these facts suggested this investigation to the author, and the object of this work has been to determine: (1) What changes take place; (2) the rate of such changes and (3) their causes.

METHOD OF PROCEDURE.

In making this investigation two samples of a water supply were taken at the same time, one of which was kept at room temperature, which averaged 18.5 degrees Centigrade, while the other was kept on ice at a temperature averaging 11 degrees Centigrade.

Simultaneous determinations of free ammonia, albuminoid ammonia, nitrites, nitrates, and oxygen consumed were made from each sample every day, five consecutive days.

CLAIMS IN THE NITROGEN COMPOUNDS OF NITRINE

It has been found in making chemical water analysis, that in order to get results which will indicate the true character of a water supply, it is necessary to make the analysis as soon after the sampling as possible and to keep the sample at a low temperature until the analysis is made. This is necessary because it has been found that the amount of the chemical water which are most positive indicators of contamination are known to vary greatly upon standing.

Consideration of these facts suggested this investigation to the writer, and the object of this work was to determine (1) What changes take place; (2) the rate of such changes; and (3) their causes.

METHOD OF PROCEDURE

In making this investigation two samples of a water supply were taken at the same time, one of which was kept at room temperature, which averaged 18.5 degrees Centigrade, while the other was kept in ice at a temperature averaging 11 degrees Centigrade. Simultaneous determinations of free ammonia, nitrite, nitrate, and organic carbon were made from each sample every day, five consecutive days.

Sampling.

The samples were collected in two litre glass stoppered acid bottles. In taking the samples of Lake Michigan water from taps in the Institute we allowed the water to run for some time before bottling. This was done in order to remove the water which had remained in the pipes any length of time so as to get a fair sample of the supply. Chicago river samples were obtained at a considerable distance from shore and at a depth of five feet. This was accomplished by sinking the bottle with a weight attached and not removing the stopper until the proper depth was reached. In all cases the bottles were completely filled so as to exclude air.

Method of Analysis.

Preparation of ammonia free water:

Realizing the importance of using water which was free from nitrogen for washing, dilution and in preparation of solutions, extra ordinary care was taken in its preparation. The apparatus used is shown in Fig. II; it offered only metallic surfaces to the action of water and steam, thus eliminating the contaminating effect which contact with organic substances would introduce. The still was made of sheet copper and held about four gallons. The condensing tubes were of block tin held in a galvanized iron jacket through which the cooling water circulated.

The samples were collected in two litre glass stoppered acid bottles. In taking the samples of Lake Michigan water from taps in the Institute we allowed the water to run for some time before bottling. This was done in order to remove the water which had remained in the pipes any length of time so as to get a fair sample of the supply. Chicago river samples were obtained at a considerable distance from shore and at a depth of five feet. This was accomplished by sinking the bottles and at a depth of five feet. The air in the bottles was removed by the proper depth was reached. In all cases the bottles were completely filled so as to exclude air.

Method of Analysis

Preparation of ammonia free water:

Realizing the importance of using water which was free from nitrogen for washing, dilution and in preparation of solutions, etc., ordinary care was taken in its preparation. The apparatus used is shown in Fig. 1; it allowed only distilled water to be added to water and steam, thus eliminating the contaminating effect which would result from organic substances we wish to introduce. The still was made of sheet copper and held about four gallons. The condensing tubes were of black tin held in a galvanneum iron jacket through which the cooling water

4

In preparing ammonia free water about 5 grams of sodium carbonate was added to the contents of the still each time and the first and last thirds of the distillate were rejected. The collecting bottle was an ordinary two litre acid bottle.

Determination of Free Ammonia.

Nessler's solution:

This was prepared by dissolving 16 grammes of mercuric Chloride in about a half litre of ammonia free water. Then 35 grammes of potassium iodide were dissolved in 200 cubic centimeters of water. The first solution was poured into the second until the precipitated mercuric iodide ceased to be redissolved on stirring, and 160 grammes of solid potassium hydroxide added. This was diluted to one litre and finally the strong solution of mercuric chloride was added, little by little until the red mercuric iodide just began to be permanent. The excess of mercuric iodide was allowed to settle to the bottom of the bottle; the color of the finished reagent was pale straw.

Standard Solution of Ammonium Chloride.

.4777 grammes of pure dry ammonium chloride were dissolved in 250 cubic centimetres of ammonia free water. After mixing thoroughly 10 cubic centimetres of this solution were taken and diluted to one half a litre with ammonia free water. 1 cubic centremetre of this solution contains ammonium chloride to correspond to .01 mgr. of nitrogen.

In preparing ammonia free water about 3 grams of sodium carbonate was added to the contents of the still each time and the first and last thirds of the distillate were rejected. The collecting bottle was an ordinary two litre acid bottle.

Preparation of Ammonia Free Water

Ammonia's definition

This was prepared by dissolving 10 grams of mercuric chloride in about a half litre of ammonia free water. Then 35 grams of potassium iodide were dissolved in 200 cubic centimeters of water. The first solution was poured into the second until the precipitated mercuric iodide ceased to be redissolved on stirring, and 100 grams of solid potassium hydroxide was added. This was diluted to one litre and filtered by the strong solution of mercuric chloride was added, little by little until the red mercuric iodide just began to be permanent. The excess of mercuric iodide was allowed to settle to the bottom of the bottle; the color of the finished reagent was pale straw.

Preparation of Ammonia Free Water

477V grams of pure dry ammonium chloride were dissolved in 200 cubic centimeters of ammonia free water. After mixing thoroughly 10 cubic centimeters of this solution were taken and diluted to one half a litre with ammonia free water. 1 cubic centimeter of this solution contains ammonium chloride to correspond to .01 gram of nitrogen.

2% Sodium Carbonate Solution:

This was prepared by dissolving 200 grammes of sodium carbonate in one litre of ammonia free water.

Nesslerization:

The process of nesslerization used is as follows: The nessler tube contains 50 cubic centimeters of water to be tested. To this one cubic centimetre of the Nessler solution was added, allowing it to drop slowly upon the surface of the water in the tube. After this addition of the reagent the liquid was allowed to stand twenty minutes to develop the full depth of color.

To estimate the amount of ammonia present in the water, comparison was made between 50 cubic centimetres of the distillate from the water under examination, and 50 cubic centimetres of water containing a known quantity of nitrogen as ammonia chloride. The standard solution was accurately measured from a pipette graduated to hundredths of a c.c. into a Nessler tube and diluted with nitrogen free water to the 50 c.c. mark. After adding 1 c.c. of Nessler solution it was allowed to stand for twenty minutes and compared with 50 c. c. of water under examination. In each determination several standard color tubes were prepared in this way each containing a different amount of ammonium chloride solution.

In making all color comparisons a black wooden box or camera was used, which cut out all side lights. This is shown in Fig. I the tubes being illuminated from the bottom by means of a mirror

REAGENTS AND SOLUTIONS

This was prepared by dissolving 300 grams of sodium carbonate

in one litre of ammonia free water.

Procedure

The procedure of determination used is as follows: The reagent

tube containing 50 cubic centimeters of water to be tested. To this one cubic

centimeter of the reagent solution was added, allowing it to drop slowly

upon the surface of the water in the tube. After the addition of the

reagent the liquid was allowed to stand twenty minutes to develop the full

depth of color.

To estimate the amount of ammonia present in the water, com-

parison was made between 50 cubic centimeters

of the distillate from the water under examination, and 50 cubic cen-

timeters of water containing a known quantity of nitrogen as ammonium chloride.

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to the 50 c.c. mark. After adding 1 c.c. of Nessler solution it was allowed

to stand for twenty minutes and compared with 50 c.c. of water under exam-

ination. In each determination several standard color tubes were prepared

in this way each containing a different amount of ammonium chloride solution.

In making all color comparisons a black wooden box or camera

was used, which cut out all side lights. This is shown in Fig. 1.

The tubes being illuminated from the bottom by means of a mirror

reflecting light from a window, the cross-section of the tubes being brought to the eye by another mirror just above the top of the tubes.

The operation of this box can be readily understood from an inspection of the three views of it previously referred to. It afforded a means of making very careful color comparisons.

Method:

A half litre of water (250 c.c. in the case of the river water because of the high nitrogen content), was rendered alkaline by addition of 5 C. C. of 20% sodium carbonate solution and distilled in an 800 C C Kjeldahl flask the apparatus being arranged as shown in Fig. III. The rate of distillation was such that 50 c. c. was collected in about ten minutes. This is important because with the utmost precaution some ammonia will be lost through imperfect condensation, and this loss will be greater in proportion as the rate of distillation is made more rapid. The amount of ammonia in the distillate being therefore a function of time employed, it becomes necessary to eliminate, so far as may be, any error that might arise from this source by conducting all distillations as nearly as possible at the same rate.

The distillate was caught in three 50 c. C/ Nessler tubes which were nesslerized separately unless the ammonia content was high, in which case the distillate was collected in a graduated 250 c c flask and after dilution to the mark and thorough mixing an aliquot part was taken for analysis. Previous to each analysis the flasks and condensers were steamed free from ammonia.

reflected light from a mirror, the cross-section of the tube being brought
to the eye by another mirror just above the top of the tube.
The operation of this box can be readily understood from an inspection
ion of the three of it previously referred to. It afforded a means
of making very careful color comparisons.

Method:

A half litre of water (200 c.c. in the case of the river water
because of the high nitrogen content), was rendered alkaline by addition of
2 c.c. of 30% sodium carbonate solution and distilled in an 800 c.c.
Kjeldahl flask the apparatus being arranged as shown in Fig. III. The rate
of distillation was such that 30 c.c. was collected in about ten minutes.
This is important because with the utmost precision some ammonia will be lost
through imperfect condensation, and this loss will be greater in proportion
as the rate of distillation is made more rapid. The amount of ammonia
in the distillate being therefore a function of time employed, it becomes
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The distillate was caught in three 50 c.c. Nessler tubes which
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which case the distillate was collected in a graduated 250 c.c. flask and
after dilution to the mark and thorough mixing an aliquot part was taken
for analysis. Provision is made to collect the flask and contents
were steamed free from ammonia.

Alkaline Potassium Permanganate Solution

Two hundred grammes of solid potassium hydroxide and eight grammes of crystallized potassium permanganate were dissolved in 1250 cubic centimetres of pure water, and boiled down to one litre.

Method:

From the residue from the determination of the free ammonia, fifty cubic centimetres of alkaline potassium permanganate solution were added, the distillate being collected either in Nessler tubes or flasks, according to the amount of ammonia present. To prevent the solution from bumping, a small amount of course thoroughly burned pumice was added. It was found that this is an excellent preventative of this trouble.

Determination of Nitrogen as Nitrates.

Method:

The method used in this determination is known as the aluminum reduction method. After consulting all the available literature it was decided to use this method as it has been universally decided that it gives the best and most reliable method and results of any.

Two and one-half cubic centimetres of a 33% solution of sodium hydroxide were added to one hundred cubic centimetres of the sample and the mixture boiled rapidly to a volume less than 50 cubic centimetres in order to drive off the free ammonia. After cooling, the residue was poured off into a tall tube, its volume made up to 50 cubic centimetres and a strip of aluminum added. After twelve hours when reduction was complete, the aluminum was removed and the tube allowed to stand until the supernatant

Alkaline Potassium Permanganate Solution

Two hundred grams of solid potassium hydroxide and eight grams of crystallized potassium permanganate were dissolved in 1250 cubic centimeters of pure water, and boiled down to one litre.

From the residue from the determination of the arsenic, fifty cubic centimeters of alkaline potassium permanganate solution were added, the residue being collected after its passage as filtrate, according to the amount of arsenic present. To prevent the solution from bumping, a small amount of coarse thoroughly burned kiesel was added. It was found that this is an excellent preventative of this trouble.

Determination of Arsenic as Arsenite

The method used in this determination is known as the aluminum reduction method. After consulting all the available literature it was decided to use this method as it has been universally decided that it gives the best and most reliable method and results of any.

Two and one-half cubic centimeters of a 3% solution of sodium hydroxide were added to one hundred cubic centimeters of the sample and the mixture boiled rapidly to a volume less than 50 cubic centimeters in order to drive off the free arsenic. After cooling, the residue was poured off into a tall tube, its volume made up to 50 cubic centimeters and a strip of aluminum added. After twelve hours when reduction was complete, the aluminum was removed and the tube allowed to stand until the subsequent

liquid was clear. A measured portion was then taken out in a pipette and placed in a Nessler tube, diluted to 50 c. c. and nesslerized as in the ammonia determination.

Determination of Nitrogen as Nitrites.

Sulphanilic Acid Solution:

One gramme of salt was dissolved in 100 cubic centimetres of hot water: Naphthylamine Hydrochloride.

Eight grammes of naphthylamine was dissolved in one litre of water and 8 cubic centimetres of concentrated hydrochloric acid added.

Standard solution of Sodium Nitrite.

To a cold solution of sodium nitrite a solution of silver nitrite was added as long as precipitate appeared. The liquid was decanted and the precipitated silver nitrite was thoroughly washed with cold water and then dissolved in boiling water. The solution was concentrated and silver nitrite allowed to crystallize from the hot solution. It was then dried between filter papers and kept in the dark.

Then .22 of dry silver nitrite was weighed out and dissolved in hot water. A slight excess of sodium chloride was then added, the liquid cooled and diluted to one litre. The precipitated silver chloride was allowed to settle and then 5 cubic centimetres of clear solution was removed and diluted to one litre. This dilution was used as a standard and it was of

and was clear. A measured portion was then taken out in a pipette and placed in a test tube, diluted to 10 c.c. and neutralized as in the ammonia determination.

Determination of Nitrogen as Nitrate

General Acid Solution

One gramme of salt was dissolved in 100 cubic centimetres of hot

water.

Eight grammes of naphthalene was dissolved in one litre of water and

8 cubic centimetres of concentrated phosphoric acid added.

Standard solution of Sodium Nitrate.

To a cold solution of sodium nitrate a solution of silver nitrate

was added as long as precipitate appeared. The liquid was decanted and

the precipitated silver nitrate was thoroughly washed with cold water and then

dissolved in boiling water. The solution was concentrated and silver nitrate

allowed to crystallize from the hot solution. It was then dried between filter

papers and kept in the dark.

The 25 of dry silver nitrate was weighed out and dissolved

in hot water. A slight excess of sodium chloride was then added, the liquid

cooled and diluted to one litre. The precipitated silver chloride was allowed

to settle and then 8 cubic centimetres of clear solution was removed and dil-

uted to one litre. This dilution was used as a standard and it was of

such a strength that 1 cubic centimetre corresponded to .001 mg. of nitrogen.

Method:

If the sample was turbid it was clarified by adding 2 cubic centimetres of both a deci normal soda solution and a deci normal alum solution. The precipitated aluminum hydroxide entangles the sediment and carries it to the bottom of the solution. For the sample 50 cubic centimetres of clear water was removed.

This was placed in a nessler jar and compared with standards to which known amounts of sodium nitrite solution had been added, the comparisons being made 45 minutes after the test solution had been added. To the 50 cubic centimetres sample 1 cubic centimetre of naphthylamine hydrochloride and 1 cubic centimetre of sulphanilic acid solution were added and allowed to stand three quarters of an hour. Simultaneously, with the addition of the reagent, were added to the water under examination, the same quantities of reagents were added to a series of solutions which contained accurately known quantities of pure sodium nitrite. If a color appeared in the sample in the course of twenty minutes to one hour after the addition of reagents, it was matched with some one of the tints produced in the series of standards, and the quantity of nitrites contained in the original water was regarded as being the same as that contained in the standard which produced the same tint. If no color developed in the course of an hour the water was regarded as being free from nitrites.

such a strength that it will be visible throughout the 1000 cc. of the liquid.

Method:

If the sample was turbid it was clarified by adding 2 cubic centimeters of both a good normal soda solution and a good normal acid solution.

The precipitated aluminum hydroxide contained the sediment and curries it to the bottom of the solution. For the sample 50 cubic centimeters of clear water was added.

This was placed in a beaker jar and compared with standards to which known amounts of sodium nitrite solution had been added, the comparisons being made 45 minutes after the test solution had been added. To the

50 cubic centimeters sample 1 cubic centimeter of naphthylamine hydrochloride and 1 cubic centimeter of phosphoric acid solution were added and it

allowed to stand three quarters of an hour. Simultaneously with the addition of the reagent, were added to the water under examination, the same

quantity of reagent was added to a series of solutions which contained exactly known quantities of pure sodium nitrite. If a color appeared in

the sample in the course of twenty minutes to one hour after the addition of reagent, it was matched with some one of the tints produced in the series of standards, and the quantity of nitrite contained in the original water was

regarded as being the same as that contained in the standard which produced the same tint. If no color developed in the course of an hour the water was regarded as being free from nitrite.

In this determination the camera previously described was found very useful on account of the very delicate tints produced by the small amounts.

Determination of Oxygen Consumed.

Standard Potassium Permanganate Solution.

.3952 grammes of the salt was dissolved in one litre of distilled water. Each cubic centimetre of such a solution will contain .1 mg. of oxygen available for oxidation in the presence of sulphuric acid.

Standard Solution of Ammonium Oxalate:

Ammonia oxalate was used in this connection because the solution is more stable than generally used solution of oxalic acid. Eight grammes of salt were dissolved in a litre of water and titrated against the standard potassium permanganate solution and the solution so diluted that both were equal in strength.

Method:

One hundred cubic centimetres of sample were measured into a three hundred c. c. flask and acidulated by the addition of 5 cubic centimetres of concentrated sulphuric acid. Ten cubic centimetres of the standard potassium permanganate were then added and the flask allowed to remain in boiling water for thirty minutes, more permanganate being added if necessary to prevent complete loss of color. The flask was then removed from the bath and a measured excess of the ammonia oxalate solution added and titrated back with the permanganate solution to just a perceptible pink color.

In this determination the same procedure was found very useful on account of the very delicate state produced by the low

Determination of Oxalic Acid

Standard Potassium Permanganate Solution

To still one in one litre of the salt was dissolved in one litre of distilled water. Each cubic centimetre of such a solution will contain 1 mg. of oxygen available for oxidation in the presence of sulphuric acid.

Standard Solution of Ammonium Oxalate

Ammonium oxalate was used in this connection because the solution is more stable than generally used solution of oxalic acid. Eight grams of salt were dissolved in a litre of water and filtered against the standard potassium permanganate solution and the solution so diluted that both were equal in strength.

Method

One hundred cubic centimetres of sample were measured into a three hundred c. c. flask and acidified by the addition of 5 cubic centimetres of concentrated sulphuric acid. Ten cubic centimetres of the standard potassium permanganate were then added and the flask allowed to remain in boiling water for thirty minutes, when permanganate being added if necessary to prevent complete loss of color. The flask was then removed from the bath and a measured excess of the ammonium oxalate solution added and filtered back with the permanganate solution to give a permanent pink color.

Analysis of Sample No. I.

Results expressed in parts per million.

Source - Tap in Armour Institute. Turbidity - Slight. Sediment - None.

Date.	Sample.	Temp.	Free Ammonia.	Albuminoid Ammonia.	Nitrates	Nitrites	Oxygen Consumed
Feb. 5-1906	I-A.	19°	.02	.026	.30	.002	2.80
" 6- "	" "	19°	.032	.020	.40	.0016	2.76
" 7- "	" "	19°	.045	.016	.45	.0009	2.70
" 8- "	" "	16.5°	.038	.015	.60	.0002	2.68
" 9- "	" "	18°	.030	.013	.74	.00	2.65
" 5- "	I-B	10°	.018	.029	.26	.0028	2.86
" 6- "	" "	11°	.024	.026	.28	.0026	2.80
" 7- "	" "	12.5°	.028	.022	.30	.0020	2.76
" 8- "	" "	11°	.030	.021	.32	.0020	2.73
" 9- "	" "	13°	.031	.019	.35	.0020	2.70



Analysis of Sample No II

Results expressed in parts per million.

Source - Tap in Armour Institute Turbidity - Slight Sediment - None.

Date	Sample	Temp.	Free Ammonia.	Albuminoid Ammonia.	Nitrates	Nitrites.	Oxygen Consumed
Feb 12-1922	II-A	20°	.024	.072	.35	.0018	2.96
" 13- "	"	18.5°	.030	.062	.40	.0012	2.90
" 14- "	"	19°	.036	.054	.40	.0008	2.86
" 15- "	"	19.5°	.020	.051	.48	.00	2.84
" 16- "	"	19°	.012	.048	.57	.00	2.80
" 12- "	II-B	10°	.020	.080	.31	.0022	3.10
" 13- "	"	9.5°	.022	.076	.36	.0020	3.06
" 14- "	"	9°	.025	.070	.37	.0016	3.00
" 15- "	"	11°	.027	.067	.42	.0016	2.98
" 16- "	"	10.5°	.029	.064	.47	.0012	2.95

Analysis of Sample No III.

Results expressed in parts per million.

Turbidity-Decided. Sediment-Much Oyster-Grass.

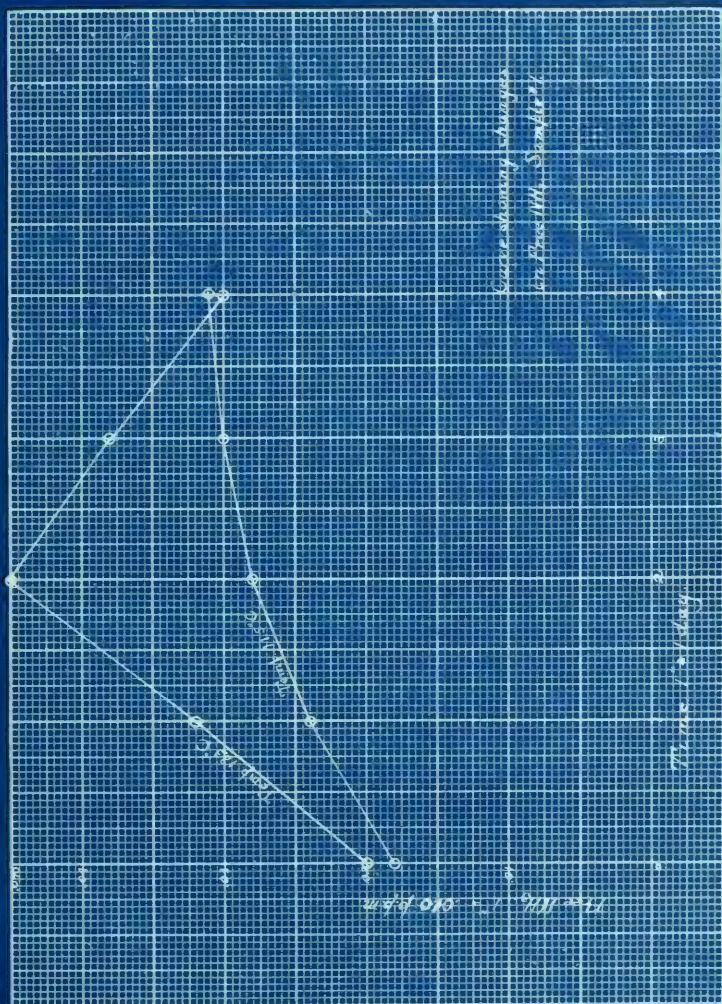
Source- Chicago River at 31st St.

Date	Sample	Temp.	Free Ammonia.	Albuminoid Ammonia.	Nitrates.	Nitrites	Oxygen Consumed
Feb. 19-1906	III-A.	19.5°	13.2	4.8	.30	.028	22.28
" 20 "	" "	18.5°	16.8	2.9	.44	.026	21.86
" 21 "	" "	19°	17.1	2.4	.48	.023	21.52
" 22 "	" "						
" 23 "	" "	18°	14.1	1.8	.52	.018	21.40
" 19 "	III-B	11°	15.0	5.4	.28	.032	24.18
" 20 "	" "	10°	17.4	5.2	.30	.030	23.90
" 21 "	" "	12.5°	19.5	4.9	.32	.026	23.72
" 22 "	" "						
" 23 "	" "	10.5°	22.6	4.6	.48	.020	23.44

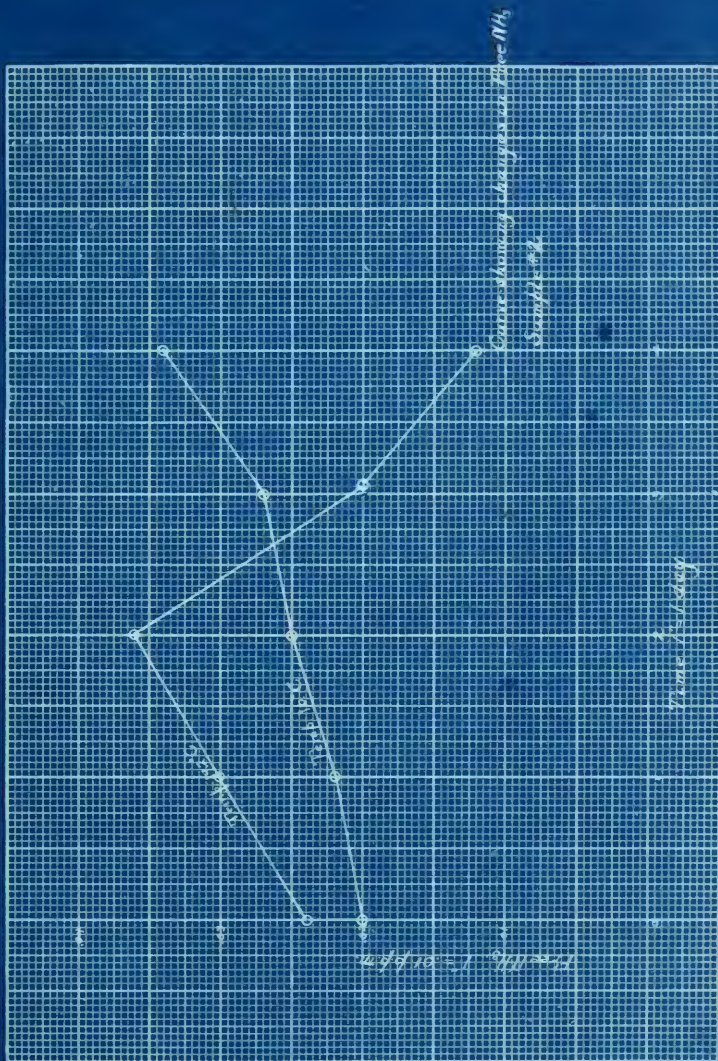
Analysis of Sample No. IV.
 Results expressed in parts per million.
 Turbidity - Decided. Sediment - Much Odor-Gassy.
 Source - Chicago River at 31st St.

Date	Sample	Temp	Free Ammonia	Aluminoid Ammonia	Nitrates	Nitrites	Oxygen Consumed
Mar 5-1906	IX - A	19°	14.2	5.2	.36	.024	26.14
" 6- "	" "	18.5°	17.2	3.8	.44	.020	25.80
" 7- "	" "	19°	18.0	3.0	.52	.018	25.52
" 8- "	" "	18°	18.6	2.0	.64	.018	25.32
" 9- "	" "	16°	17.2	1.2	.70	.014	25.16
" 5- "	IX - B	12°	16.4	5.5	.32	.030	26.76
" 6- "	" "	11°	19.2	5.0	.42	.026	26.32
" 7- "	" "	11.5°	21.6	4.4	.48	.020	26.02
" 8- "	" "	10°	23.2	4.0	.58	.016	26.00
" 9- "	" "	11°	25.0	3.8	.68	.012	25.96





WALSH DISTINGUISH CO., CHICAGO



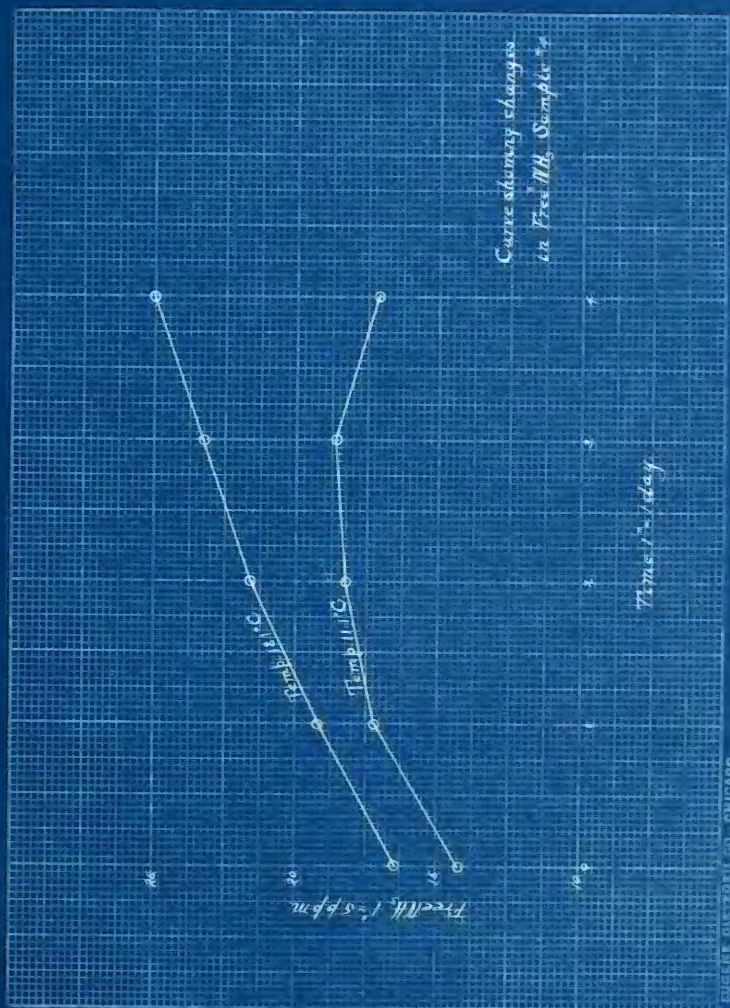
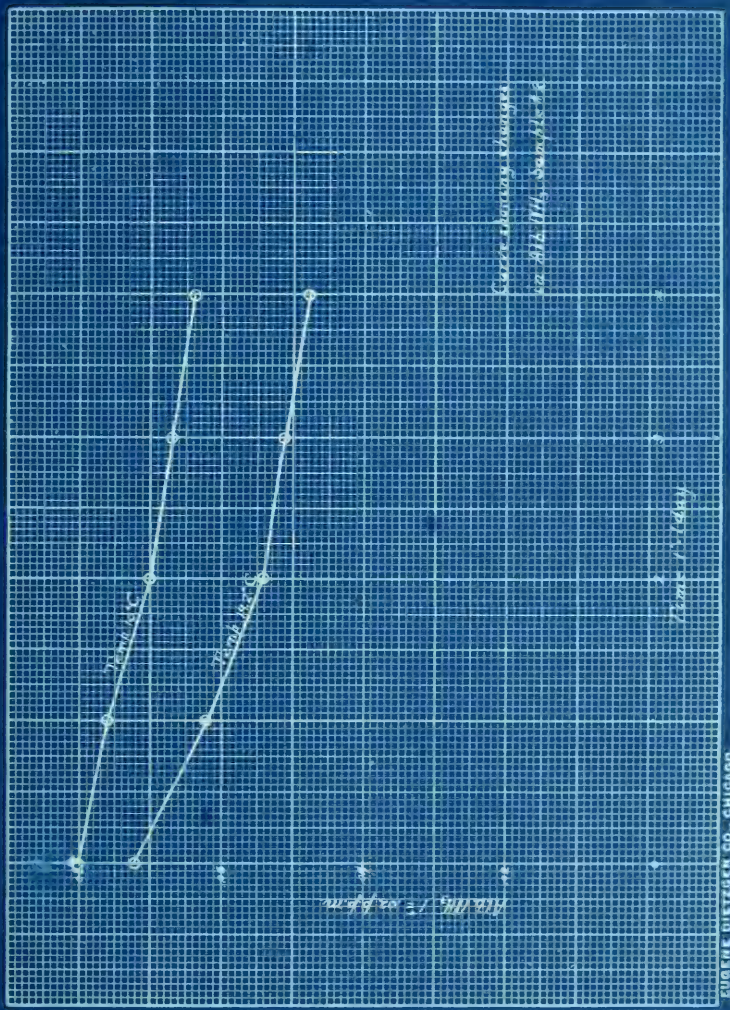
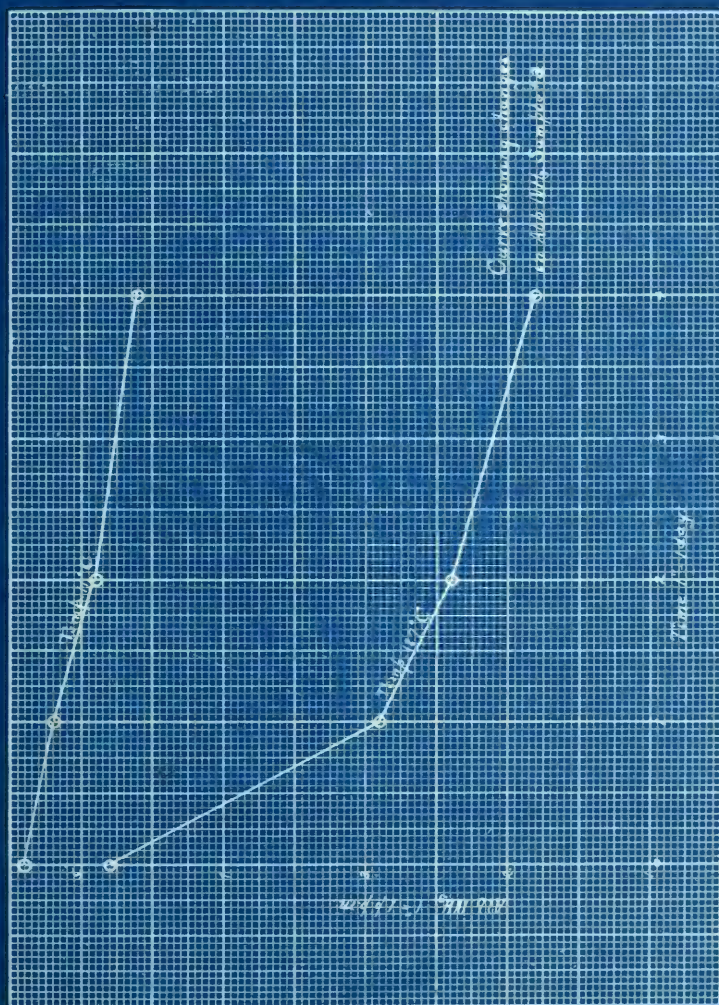


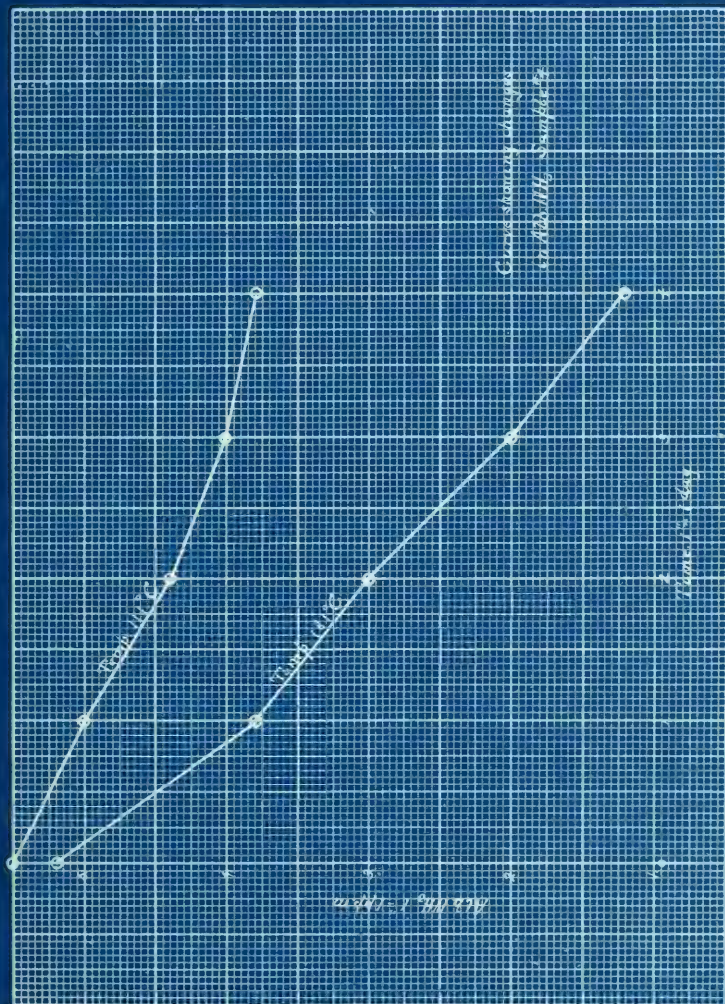
FIGURE ON TIGHT CO. CHICAGO

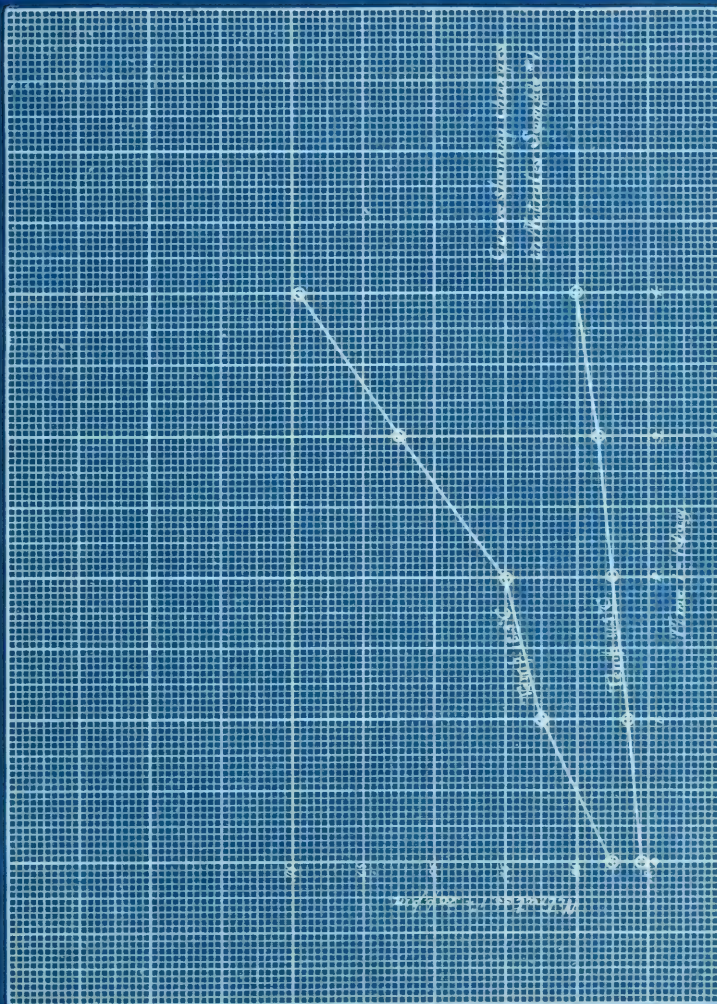




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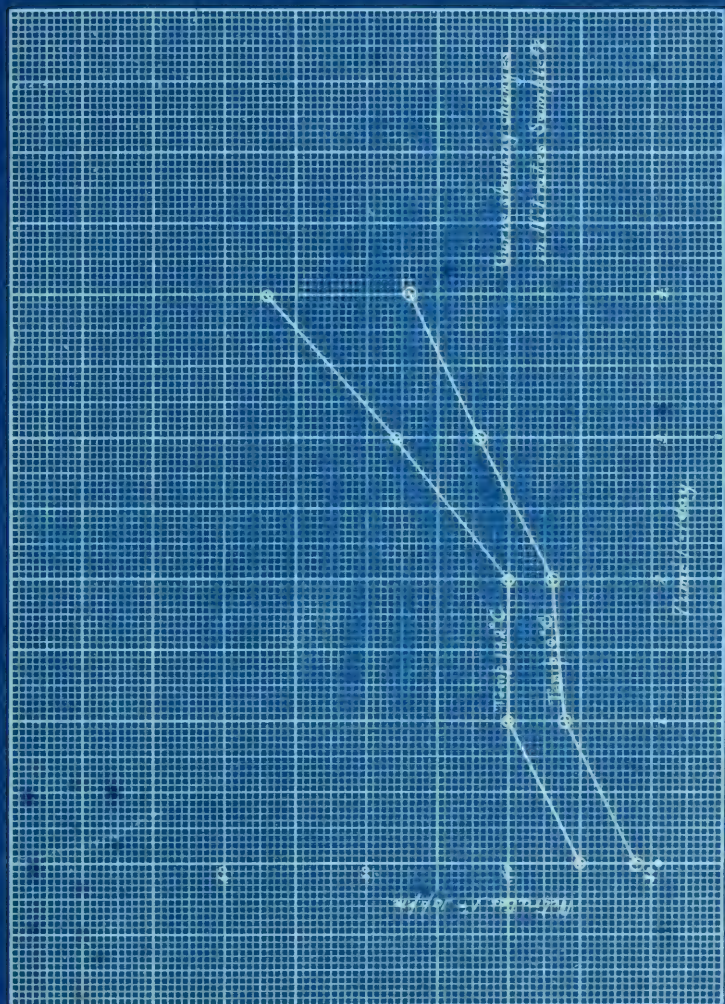






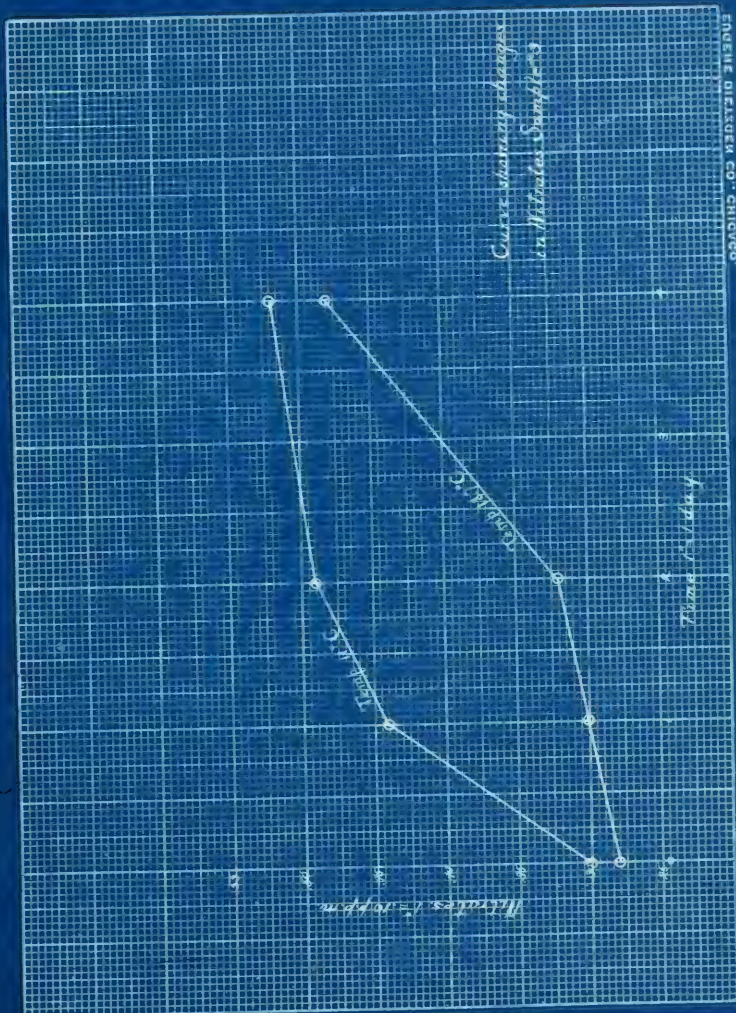
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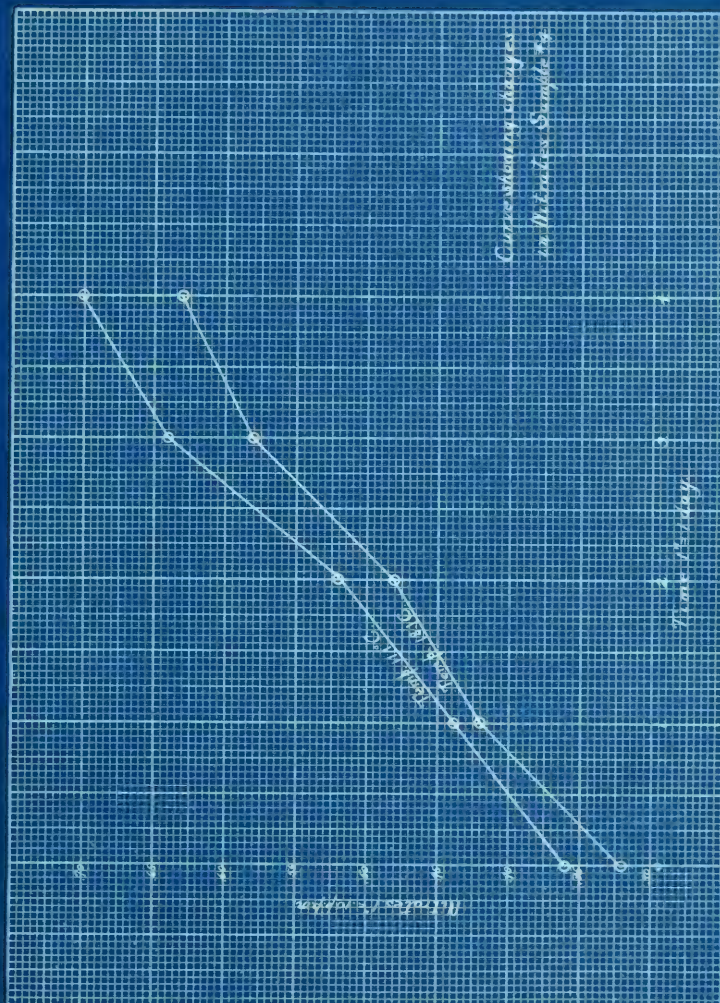


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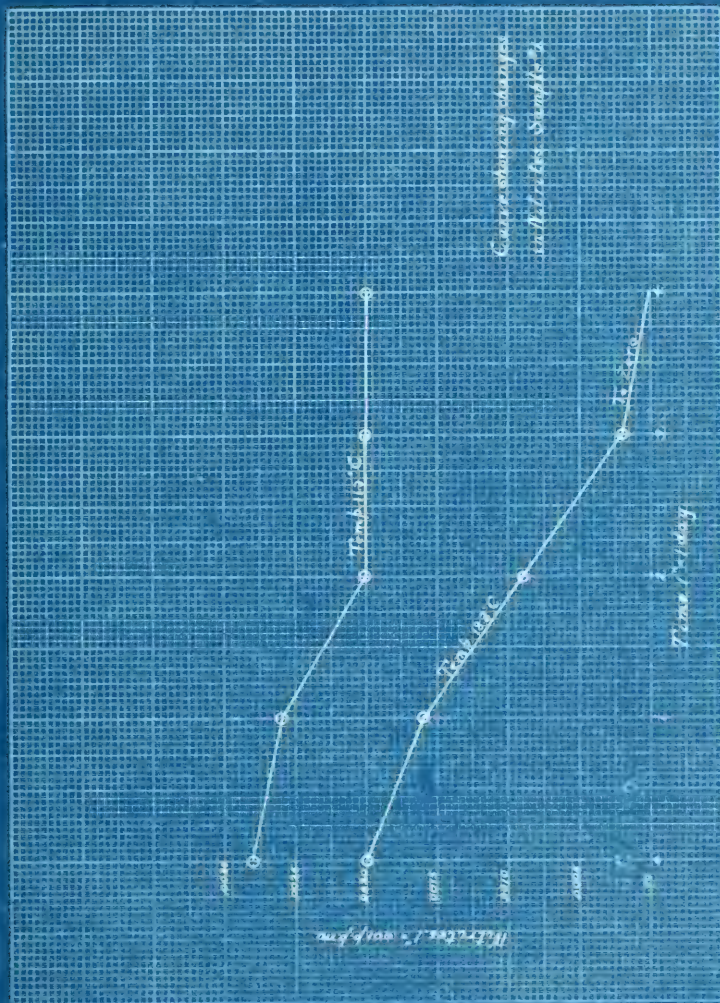












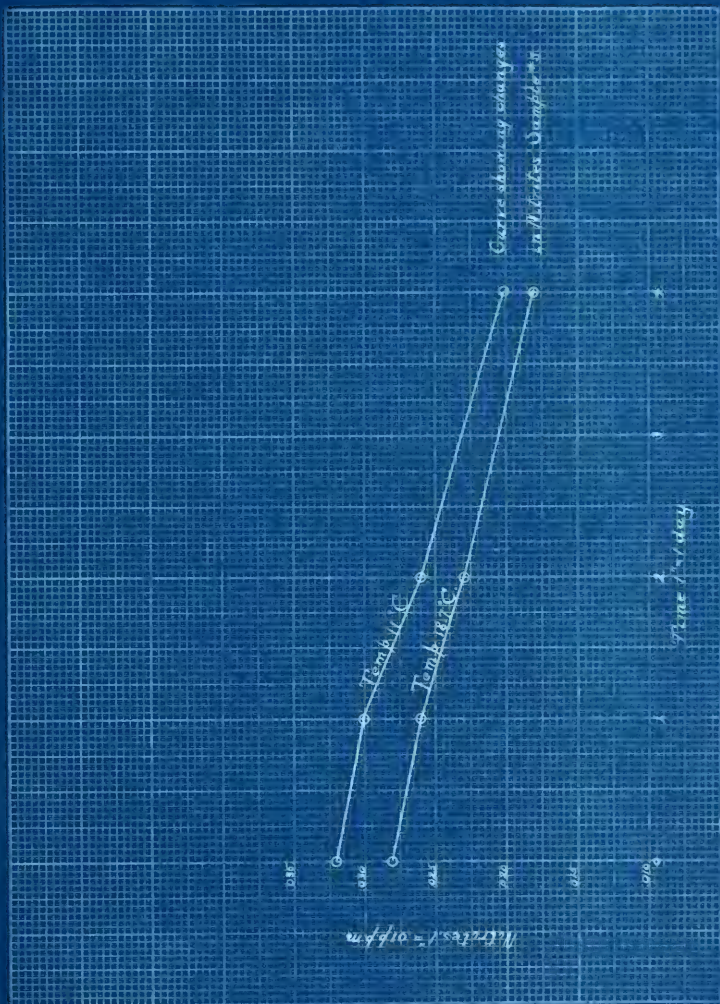
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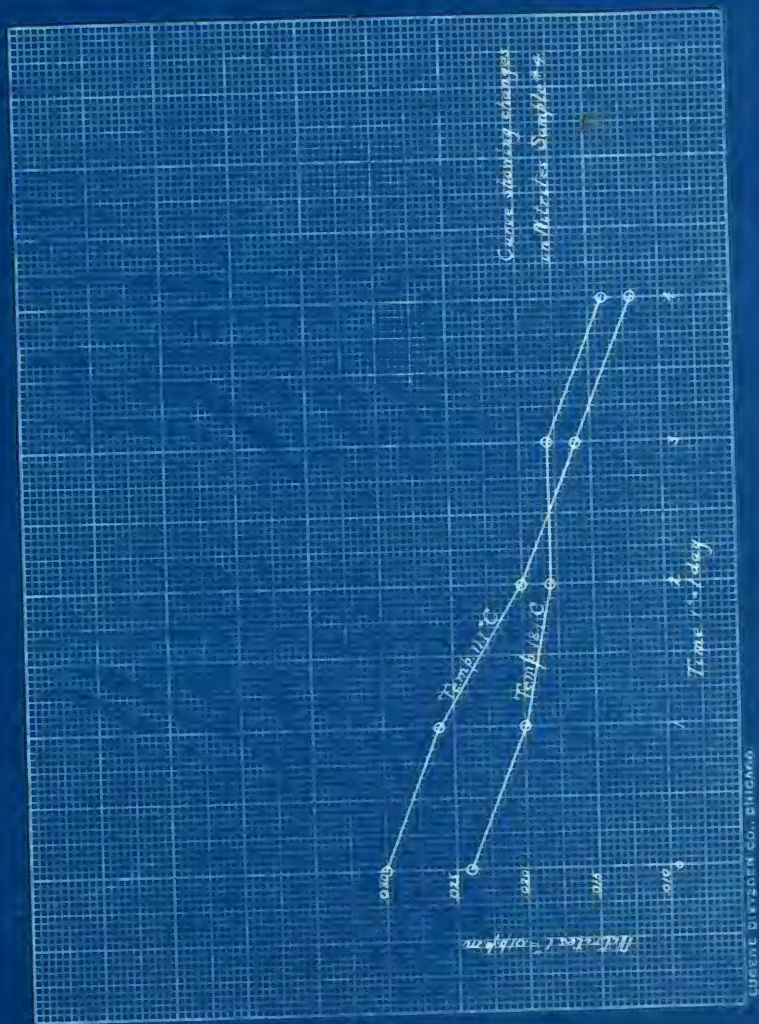
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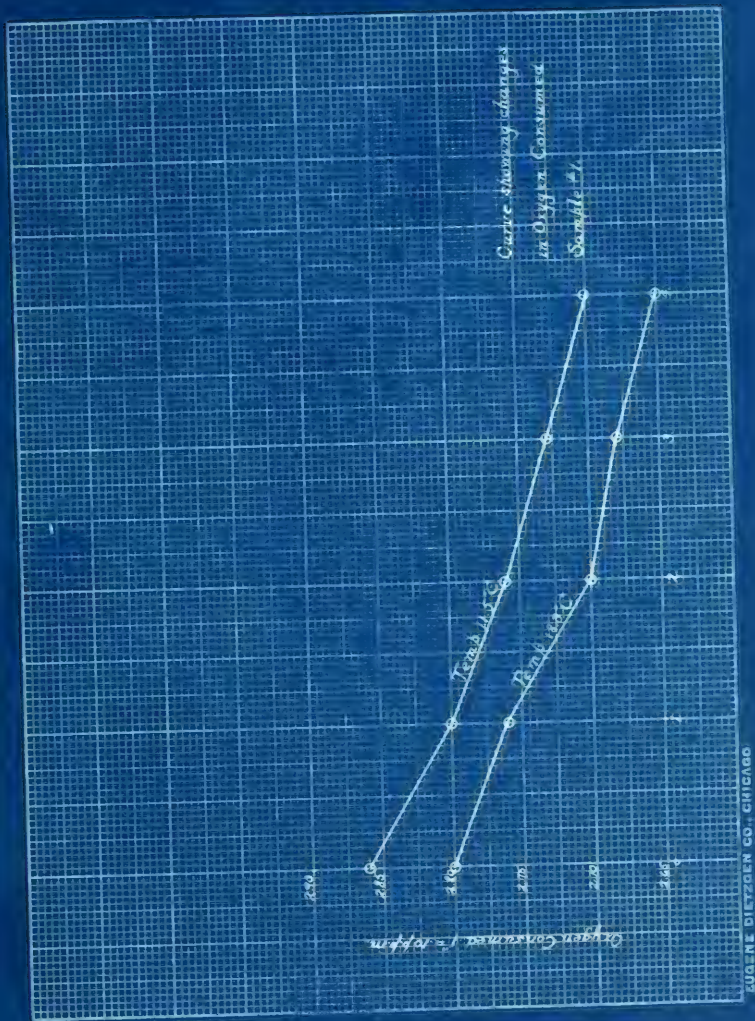


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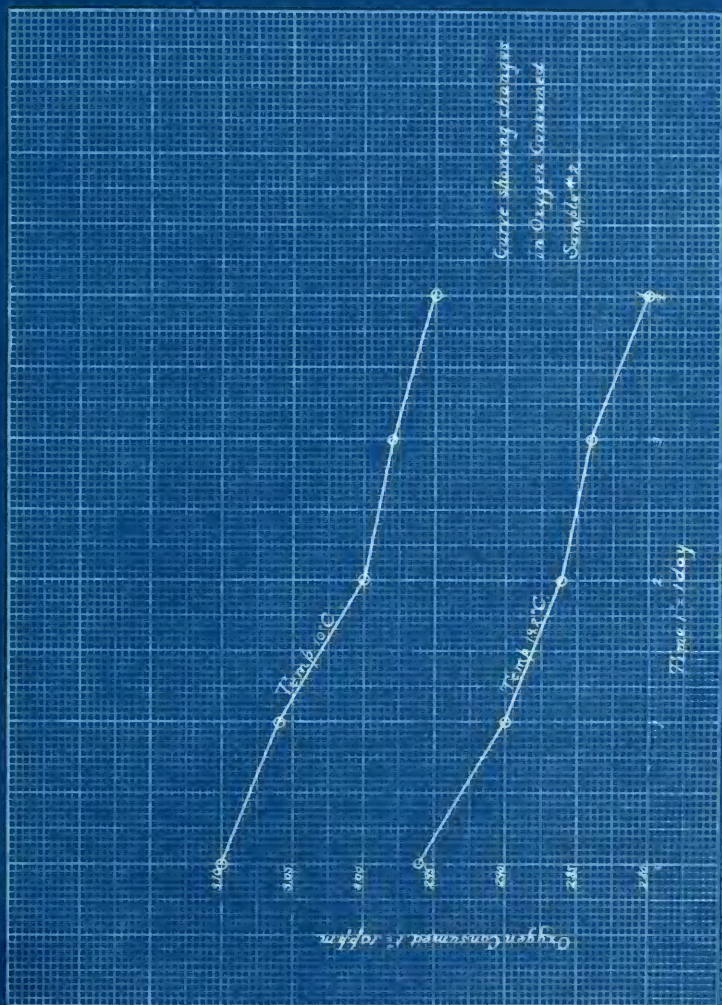




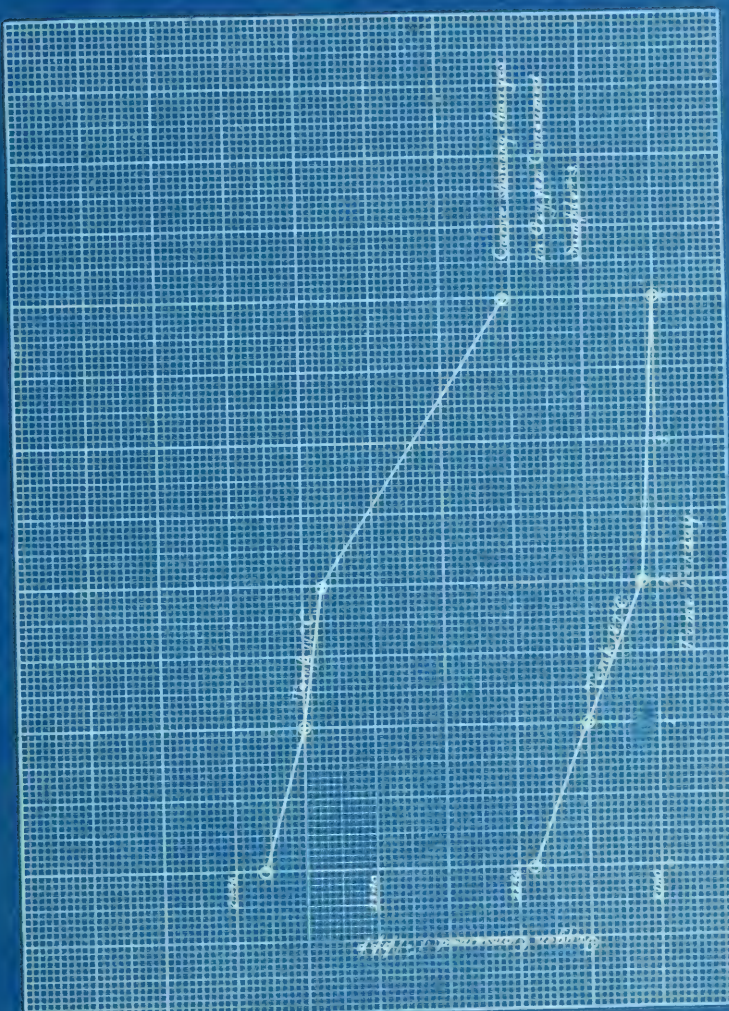












LORENZ DIETZGEN GbR, CHICAGO



Discussion of Results.

The results obtained were tabulated and appear on pages 11 to 14 inclusive. The samples designated "A" is the one which remained at room temperature while the one "B" is the one which was kept on ice.

Curves were plotted for each constituent of all waters, the ordinates representing the amount of each and the abscissae representing lapse of time. This method was selected as the best adapted to show the changes which took place and by placing the curves for both samples on one sheet the effect of temperature is best seen. The curves are shown on pages 15 to 37 each one being suitably labelled to describe what it represents.

Free Ammonia:

By examining the curves for this constituent for all samples it is observed that the amount steadily increases in the ice-box sample. In the room temperature sample the content increases steadily up to a maximum on the third day and decreases from that point on. The curves also show that the changes take place more rapidly in the sample of higher mean temperature. The rate of change varies directly as the content as is seen by comparing the results for a sample with a high content with one of lower content. On account of this no quantitative value of the rate of change can be stated as it is seen that it is a function of the amount of the constituent.

Discussion of Results.

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Interpretation

By examining the curves for this constant for all samples it is observed that the amount steadily increases in the ice-box samples. In the room temperature sample the content increases steadily up to a maximum on the third day and decreases from that point on. The curves also show that the changes take place more rapidly in the sample of higher room temperature. The rate of change varies directly as the content as is seen by comparing the results for a sample with a high content with one of lower content. On account of this no quantitative value of the rate of change can be stated as it is seen that it is a function of the amount of the content.

In general it may be said that the amount of free ammonia increases with the time. The exception pointed out above in the sample kept at room temperature is due to the fact that after the third day the free ammonia began oxidizing to nitrites thus reducing it's value. The usual increase is due to the changing of albuminoid ammonia to free ammonia, this being a well known step in the cycle of the changes of the the nitrogen constituents. No quantitative value of velocity of this or other changes is possible for water in general, because the rate of change is a function of the utmost amount of the constituent itself as well as of outside conditions.

Albuminoid Ammonia.

Inspection of the curves shows that this constituent decreases steadily in amount, due to the fact that it is changing to free ammonia as previously stated. This change is affected by action of heat, air and bacteria. The room sample shows a greater rate of change than the colder sample due to the increased action of the higher temperature. This is one of the prime factors which cause the change of condition and it's effect is to increase the number of bacteria which are active in producing the change. As with free ammonia the actual amount of decrease per unit time is greatest in samples having the highest content.

Nitrites:

The only available waters for examination had such a

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producing the change. As with free ammonia the actual amount of

decrease per unit time is greatest in samples having the

highest content.

Microbes

The only available means for examination had such a

low amount of nitrites that it was not possible to get reliable results. Both samples showed a continually decreasing content, with the warmer sample changing more rapidly as in previous cases. Inasmuch as this constituent decreases steadily it shows that the change from nitrites to nitrates goes on faster than that from free ammonia to nitrites. This may be expected as the later change necessitates a much greater oxidation than the former.

Nitrates.

The results obtained for nitrates show that they steadily increase in value, the change taking place more rapidly in the warmer sample. This is the last step in the cycle of changes that the nitrogen constituents undergo, the order of change being as follows: album. ammonia to free ammonia; free ammonia to nitrites; nitrites to nitrates.

The amount of nitrates present in the room sample was always higher than the ice-box sample. This, as well as the greater rate of change is due to the fact that more free ammonia and nitrites are present in the warmer sample at any one time so that material for oxidation is greater.

Oxygen Consumed.

This is the quantity of oxygen required for burning of organic matters contained in water, or rather the quantity of oxygen required for oxidation of readily affected organic materials present; for, as it is well

For amount of nitrogen that it was not possible to determine. The results showed a continuously decreasing content, with the number sample being more rapidly as in previous cases. Inasmuch as this consistent decrease steadily it shows that the change from nitrogen to nitric acid on faster than that from free ammonia to be nitrified. This may be expected as the latter change necessitates a much greater oxidation than the former.

Discussion

The results obtained for nitrogen show that they steadily increase in value, the change being more rapidly in the former sample. This is the last step in the cycle of changes that the nitrogen compounds undergo, the order of change being as follows: albumin, ammonia to free ammonia; free ammonia to nitrified; nitrified to nitric acid. The amount of nitrogen present in the room sample was always higher than the ice-box sample. This, as well as the greater rate of change is due to the fact that more free ammonia and nitrified are present in the room sample at any one time so that material for oxidation is greater.

Conclusions

This is the quantity of oxygen required for burning of organic matter contained in water, or rather the quantity of oxygen required for oxidation of readily oxidized organic materials present; for, as it is well

known not all of the organic matters are affected by chemical processes employed.

The results show that this constituent gradually diminishes in value because the amount of oxidizable matter is continually decreasing due to the change of albuminoid to free ammonia. The amount present in any sample was always highest in the colder sample because here the oxidizable matter available is higher.

The following citations of references will point out the many possible causes of the changes observed. Any or all may take place in a water sample which is to be analyzed as well as in the supply itself. The fact is, that changes do take place and do so with considerable rapidity as shown by this investigation, and too much stress cannot be laid upon the desirability of making analyses as soon after sampling as possible.

"Very few natural matters are found which do not contain some trace of ammonium salts. Except in acid rain and moorland water, it probably always exists as ammonium carbonate. By the distillation of such waters with or without the addition of a little alkali the ammonia is carried over in distillation and is spoken of as "free ammonia" to distinguish it from a further quantity of ammonia, which can be obtained by adding a strong alkaline solution of potassium permanganate and continuing the distillation. This latter quantity is spoken of as the "albuminoid ammonia", a term which is misleading since this ammonia does not exist in water but is produced by the decomposition of nitrogenous organic matter by alkali permanganate."

known that all of the organic matter was utilized in chemical processes employed.

The results show that this constant gradually diminished in value because the amount of available matter is constantly decreasing due to the change of aluminoid to free ammonia. The amount present in any sample was always abundant in the water sample because the available matter available is higher.

The following citations of references will point out the many possible causes of the changes observed. Any or all may take place in a water sample which is to be analyzed as well as in the supply itself. The fact is that changes do take place and do so with considerable rapidity as shown by this investigation and too much stress cannot be laid upon the desirability of making analyses as soon after sampling as possible.

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"In the animal body nitrogen is present chiefly in the form of proteids and their derivatives the albuminoids, e. g. mucin, gluten, keratin, elastin, as well as other highly complex bodies such as lecithin, haemoglobin, but, in addition, the animal gives off in its secretions and excretions a number of nitrogenous compounds."

"In the decomposition of nitrogen organic matter on exposure to oxygen the carbon is first oxidized; this leaves the nitrogen in the form of ammonia, which under favorable conditions, is still further oxidized into water and nitric acid. It is not intended to be asserted that all the carbon must be oxidized before nitrification can begin; without doubt the two actions go on coincidentally. But in general, this order of oxidation is observed, not only when there is a smaller amount of oxygen present than would suffice for the complete decomposition."

"The process of the decay of organic matter, whereby it is converted into inorganic matter through the action of oxygen, is one with which we are all familiar, in a general way through personal observation. The two extremes, living organized matter on the one hand and inert mineral matter on the other, are sharply contrasted to each other. Oxidation of organic matter, such as we have under consideration, does not go on in nature without the presence of bacteria even though the supply is limited."

By chemical means such as the use of nitric acid, potassium permanganate and the like, we can break up the organic matter and accomplish its partial oxidation. The effect of the oxidizing agents however is limited to the carbon, hydrogen, and sulphur of the organic compounds and does not extend to the nitrogen. Ammonia is invariably formed when

"In the animal body nitrogen is present chiefly in the form of proteins and their derivatives the nucleic acids, or as urea, creatinine, creatin, etc., as well as a few highly complex bodies such as lecithin, phospholipids, but, in addition, the animal gives off in its secretions and excretions a number of nitrogenous compounds."

"In the decomposition of nitrogen organic matter on exposure to oxygen the carbon is first oxidized to carbon dioxide in the form of carbon dioxide, which under favorable conditions, is still further oxidized into water and nitric acid. It is not unusual to be asserted that all the carbon must be oxidized before nitric acid can be formed; but the two notions go on coincidentally. But in general, this order of oxidation is observed, not only when there is a smaller amount of oxygen present than would suffice for the complete decomposition."

"The process of the decay of organic matter, whereby it is converted into inorganic matter through the action of oxygen, is one with which we are all familiar, in a general way through personal observation. The two extremes, living organisms and the one hand and inert mineral matter on the other, are sharply contrasted to each other. Oxidation of organic matter, such as we have under consideration, does not go on in nature without the presence of bacteria even though the supply is limited."

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found when nitrogenous organic matter is thus treated. Except when we have the action of nascent oxygen, as in the galvanic decomposition of water, we may say that the oxidation of organic matter requires the presence and vital activity of bacteria."

"A series of experiments extending over a period of several years was carried on to determine the influence of various substances in the process of nitrification. Résumé of the results is as follows: when raw sewage is made slightly acid nitrification is stopped almost; still a small amount of both nitrites and nitrates are formed. Common salt interferes with nitrification, but it is not yet clear whether there is a loss of nitrogen during the nitrification in the presence of sugar; sugar interferes at least."

"It is very probable that practically the whole of the nitrites found in water is derived from oxidation of nitrogenous matter of animal origin. Vegetable matter by oxidation in the soil yields very little acid while animal matter yields a large amount. The nitrogenous bodies of animal origin readily decomposing, probably the whole of the nitrogen ultimately becomes converted into nitric acid, which reacting upon the carbonates in the soil forms the nitrates found in sub-soil and deep well waters. No doubt there are several stages in this decomposition, some being due to the action of the bacteria found in soil, and others merely to chemical action. The breaking down of proteid matter results first in the formation of ammonia: this is converted into nitrous acid by nitrifying organisms and further oxidation lead to the formation of nitric acid.

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first in the formation of ammoniac; this is converted into nitrous acid

by nitrifying organisms and further oxidation leads to the formation

of nitric acid.

Nitrifying organisms in the absence of a free supply of oxygen reduce nitrites and if and only if there is nitrogenous organic matter also present, they produce ammonia. Nitrites are said to be found at first, but a minute quantity only is discoverable and this quickly disappears. Where nitrates are in the process of formation or reduction, traces of nitrites are found, hence some analysts lay great stress upon the presence of nitrites."

"Nitrites are nearly always found in sewage effluents from the so-called bacteria beds. Their presence indicates the sewage is undergoing active oxidation or nitrification and that the known process is not complete. They may exist in a water because conditions do not favor complete nitrification of the ammonia."

"By no known process can the amounts of organic matter in solution in potable water be estimated with any approach to accuracy. As organic matter of vegetable origin is of little significance, most of the tests in the analysis of water are for the purpose of attempting to differentiate between it and animal contamination. Some tests while not professing to differentiate between the two, indicate whether the water contains any readily oxidizable matter or not."

"Potassium nitrate in 1/2 % solution containing 5% of peptone was reduced to nitrites by 85 of the 100 varieties examined. Fifty varieties destroyed nitrites, four of them liberating free nitrogen. Many bacteria which reduced nitrates without liberation of nitrogen, had very little or

Nitrifying organisms in the absence of a free supply of oxygen reduces nitrite and it may be that in nitrifying organic matter also present, their products combine. Nitrites are said to be found at first, but a minute quantity only is discernible and this quickly disappears. Where nitrites are in the process of formation or reduction, the traces of nitrite are found, hence some analysis for traces of nitrite upon the presence of nitrite."

"Nitrites are normally always found in sewage effluents from the so-called bacteria beds. Their presence is indicative of the sewage is undergoing active oxidation or nitrification and that the known process is not complete. They may exist in a water because conditions do not favor complete nitrification of the ammonia."

"By no known process can the amounts of organic matter in solution in potable water be estimated with any approach to accuracy. In organic matter as vegetable origin is of little significance, most of the tests in the analysis of water are for the purpose of attempting to differentiate between it and animal excretion. Some tests will not distinguish between the two, others the water contains no readily oxidizable matter or not."

"Potassium nitrate in 1/2% solution containing 1% of peptone was reduced to nitrite in 10 to 100 minutes at 37°C. Nitryl variation destroyed nitrites, four of them liberating free nitrogen. Many bacteria which reduced nitrate without liberation of nitrogen, had very little or

no effect on nitrates and nitrites are attacked by microbes which have no effect when proteids are present/.

The so called denitrifying organisms destroy nitrates independent of the nature of the nutritive solutions, whilst the others act only in the presence of certain carbon compounds. The action of both classes of microbes is retarded by the presence of highly oxygenated compounds, such as chlorates without injury to their growth."

In conclusion it can be stated that no matter what produces these changes it is manifest that they actually take place, and even after a few days standing the changes may be so marked as to completely mask the true nature of the sample under examination. Inasmuch as it is usually impossible to make the analysis immediately upon sampling, due to the fact that the laboratory is sometimes at a great distance from the source of supply, it would probably bring about a uniformity of interpretation of results if all analysts agreed upon a certain time after sampling when the analysis should be made. Then from a more elaborate investigation upon the lines of this one, the condition of the water in its original state might be determined/.

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